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13. ABSTRACT (Maximum 200 words) The purpose of this work was to optimize the reinforcing effect provided by liquid crystalline polymers (LCP) when combined with thermoplastics. The first phase of the research was concerned with the generation of in situ composites in which the LCP fibrils are directly generated during processing. Because the formation of in situ composites requires extensional deformation, the fibrils are highly oriented in one direction leading to materials with highly anisotropic mechanical properties. Methods for reducing the mechanical anisotropy of in situ composites were studied next. The desire to reduce the mechanical anisotropy lead to pregeneration of LCP fibrils using a novel dual extrusion technique developed in our laboratory. The materials containing the pregenerated microfibrils, referred to as microcomposites, were then processed at temperatures where the LCP fibrils were not melted. The mechanical anisotropy of injection molded microcomposites were reduced. Further details of the work carried out in this research are given below. First, the research concerned with the in situ composites is discussed. This is followed by a discussion of the process for generating the microcomposites. Finally the processing studies on the microcomposites is presented.					
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PROCESSING STUDIES ON COMPOSITES BASED ON BLENDS OF THERMOTROPIC LIQUID CRYSTALLINE POLYMERS WITH THERMOPLASTICS

FINAL REPORT

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SEPTEMBER 22, 1994

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A. Statement of the Problem Studied

The purpose of this work was to optimize the reinforcing effect provided by liquid crystalline polymers (LCP) when combined with thermoplastics. The first phase of the research was concerned with the generation of in situ composites in which the LCP fibrils are directly generated during processing. Because the formation of in situ composites requires extensional deformation, the fibrils are highly oriented in one direction leading to materials with highly anisotropic mechanical properties. Methods for reducing the mechanical anisotropy of in situ composites were studied next. The desire to reduce the mechanical anisotropy lead to pregeneration of LCP fibrils using a novel dual extrusion technique developed in our laboratory. The materials containing the pregenerated microfibrils, referred to as microcomposites, were then processed at temperatures where the LCP fibrils were not melted. The mechanical anisotropy of injection molded microcomposites were reduced.

Further details of the work carried out in this research are given below. First, the research concerned with the in situ composites is discussed. This is followed by a discussion of the process for generating the microcomposites. Finally the processing studies on the microcomposites is presented.

B. In Situ Composites

This part of the work addresses a number of questions regarding the use of thermotropic liquid crystalline polymers (TLCP's) to reinforce thermoplastics. In particular we concentrate on the effect of partial miscibility between the matrix and the TLCP, the effect of the properties exhibited by the TLCP itself, and why the properties of the blends pass through a maximum at an intermediate composition. Blends of an immiscible (Vectra A900) and partially miscible (HX1000) TLCP with a polyetherimide (PEI) were injection molded into mini-tensile bars and rectangular plaques, and their mechanical properties were evaluated. Interfacial, rheological, and morphological properties along with molecular orientation analysis were carried out in order to

explain the mechanical properties of the blends. Mechanical tests showed that both the tensile and flexural modulus deviate positively from the law of mixtures. However, for the PEI/HX1000 system the deviation from the law of mixtures appeared at lower TLCP concentrations compared to the PEI/Vectra A900 system. Morphological tests showed that finer higher aspect ratio TLCP fibers developed in the PEI/HX1000 system relative to the PEI/Vectra A system. In addition, both blends showed a maximum in the tensile modulus at 90 wt% TLCP. Rheological tests indicated that for TLCP-rich compositions, a higher viscosity was observed for the blends in comparison to the neat TLCPs. Therefore, due to a greater viscosity, higher magnitudes of stresses, consequently inducing a higher degree of molecular orientation, were experienced by the blends relative to the neat TLCPs. Although partial miscibility seemed to affect more strongly the stiffness of the in situ composite, the ultimate properties of the TLCP strongly dominated the ultimate properties of the PEI/TLCP composite. Mechanical tests showed that the ultimate properties of Vectra A were at least twice those of HX1000. Consequently, for TLCP-rich compositions, higher values of toughness, elongation at break and tensile strength were observed for PEI/Vectra A blends compared to PEI/HX1000 blends. This seems to suggest that the selection of a TLCP to reinforce a polymeric matrix is not only dependent upon whether partial miscibility or compatibility between the TLCP and matrix polymer exist, but also on the mechanical properties of the TLCP.

Injection molded and extruded samples of blends of a polyetherimide with thermotropic liquid crystalline polymers were subjected to uniaxial, planar and biaxial elongation deformations in order to assess the ability of these types of shearfree flows in reducing the mechanical anisotropy of the situ thermoplastic composites. The effects of these types of flow on the morphology and overall mechanical properties of the blends were also addressed. In the case of injection molded plaques, in which the initial morphology was that of fibers and droplets, the direction of the applied deformation relative to the initial direction of the TLCP fibrils was an important factor in affecting the resultant morphology and corresponding mechanical properties of the blends. If the direction of the applied uniaxial deformation was parallel to the initial fiber direction, the deformation tended to increase the average aspect ratio of the TLCP fibers and mechanical properties were enhanced along the direction of deformation. However, if the deformation was applied transverse to the initial fiber direction, the fibers tended to follow the

deformation and a 90 degrees rotation was observed. In terms of mechanical properties, an increase in the transverse direction properties accompanied by a reduction in the flow direction properties followed the realignment of the fibers. In addition, equal flow and transverse mechanical properties (reduced mechanical anisotropy) appeared at 0.5 units of transverse uniaxial strain.

In the case of planar deformation, a spreading of the fibers in the plane of deformation and a ribbon-like morphological structure were observed. However, at comparative magnitudes of planar strains, transverse planar compression tends to promote a greater spreading of the fibers relative to planar compression applied parallel to the initial direction of the fibers. In addition, planar stretching applied in a direction perpendicular to the initial direction of the TLCP fibers was effective in reducing the mechanical anisotropy of the molded plaques. Samples showing equal flow and transverse properties were obtained when planar strains greater than 0.5 units were applied in a direction perpendicular to the initial direction of the fibers. In the case of extruded sheets, in which the initial morphology was that of drops, it appeared that partial miscibility was an important factor in affecting the final morphology of the sheet. For the immiscible PEI/Vectra A system, longer and more stable TLCP fibrils were found compared to PEI/HX1000 system. It is believed that, due to lower interfacial tension, stress induced fiber breakup occurred during stretching of the PEI/HX1000 blend.

The use of in situ thermoplastic composites based on blends of a polyetherimide with an amorphous and a semicrystalline liquid crystalline polymer in the thermoforming process was also explored. Injection molded and extruded samples, in which the initial morphology of the dispersed TLCP phase was either in the form of fibers or droplets, were subjected to thermoforming. It was found that in the case where the initial morphology of the dispersed TLCP phase was that of droplets, the elongational stresses generated during forming were capable of deforming the TLCP phase into fibers, and the aspect ratio of the fibers was increased with depth of draw. However, when the initial morphology of the TLCP phase was in the form of fibers, then the relative alignment of the fibers with respect to the forming direction was an important factor in affecting the final structure of the TLCP phase in the formed tray. When the fibers were aligned parallel to the forming direction, the elongational strains generated during forming tended to further increase the aspect ratio of the fibers. In the case where the initial TLCP fibers were

aligned transversely to the forming direction, the fibers tended to spread into a ribbon-like structure after forming. Pre-stretching of the samples prior to thermoforming tended to contribute to an increase in the aspect ratio of the TLCP fibers. As a result, an enhancement in the deflection resistance of the pre-stretched/formed samples was observed. In situ thermoplastic composites seemed to be advantageous compared to glass reinforced thermoplastics in thermoforming applications. The elongational stresses generated during forming tended to deform the TLCP phase into a specific morphology. Depending on the relative direction of the deformation, either fibers or a ribbon-like structure may be developed. This is in contrast to glass reinforced PEI, in where breakage of the glass fibers occurred upon forming, which may contribute to a reduction in the mechanical performance of glass reinforced materials.

C. Microcomposites

The overall objectives of this part of work were to improve a dual extrusion process (DEP) which is used in the production of strands produced from blends of thermotropic liquid crystalline polymers (TLCPs) and thermoplastics, determine the mechanism by which TLCP morphology is developed in the DEP and to determine the optimal properties possible in composite material generated from the blends. The DEP consisted of two single screw extruders within which the TLCP and matrix material were plasticated separately. The two continuous polymer streams were joined and then mixed in a series of static mixing elements. Composite materials, referred to as microcomposites, were formed from pelletized pregenerated strands by processing at temperatures below the melting point of the TLCP.

The DEP was improved by the addition of a gear pump to the TLCP stream, multiple port phase distribution system, static mixing design, minimization of residence time, die design, and introduction of thermal control over the entire strand production process. The TLCP material was introduced into the matrix phase by means of a multiple port phase distribution system which injected twelve individual streams of TLCP into the matrix material parallel to the matrix flow direction. This method of TLCP introduction showed improvements in the axial continuity of the TLCP phase during mixing as compared with the single T-injection system.

Both Kenics and Koch static mixer designs were used and it was found that the most stable strand materials were formed when the die was designed with respect to the flow exiting the static mixing elements. For example, a dual strand die with each capillary having an L/D ratio of 1 produced the most stable strand when used with Kenics mixing elements. Finally, it was found that drawing the molten strand in a vertical drawing chimney provided a favorable thermal environment and resulted in much higher draw ratios and high mechanical properties of the strand.

The development of the reinforcing morphology in the DEP was investigated by using HX1000 in a matrix of PP. The purpose was to determine if a DEP could be used to generate a fibrillar TLCP morphology in drawn strands where blending in a single screw extruder could not. Specifically, a low concentration of TLCP (5.0 wt%) was used so that the occurrence of coalescence in the mechanism of the TLCP fibril formation could be curtailed. It was found that blending in a single extruder resulted in large axial concentration variations and a poor morphology for mechanical properties enhancement. The addition of static mixing elements to the single extruder resulted in droplets of TLCP that provided little reinforcement to the matrix material. In contrast blends produced in the DEP, with an appropriate mixing configuration, exhibited an axially continuous TLCP morphology which developed at the onset of mixing in the phase distribution system and was subsequently refined as the melt passed through the static mixing elements. The axially continuous morphology seen at the entrance of the die was maintained and further developed as the blend contracted into the capillary die and was drawn as a strand. The fibrillar TLCP morphology resulted in drawn strands with tensile properties significantly improved over strands produced through blending in a single screw extruder.

The optimal properties of composite materials was investigated by using HX1000 and Vectra B950 to reinforce a thermoplastic matrix of polypropylene (PP). The goal was to pregenerate the optimal TLCP reinforcement in the PP then process the material at a lower temperature than the melting point of the TLCP to form a composite structure. Initial studies indicated that injection molding and sheet extrusion of the pelletized strands caused the TLCP phase to agglomerate and deform which resulted in a reduction of the potential mechanical property enhancement. However, the TLCP fibrillar morphology of the pregenerated strands was maintained during compression molding which resulted in uniaxial composites with properties

equal to or greater than the properties of the strands. In addition, composites were made using a compression molding process in which strands were randomly oriented prior to consolidation in order to show the limits of properties possible in composites produced from the pregenerated strands. It was found that this process could be used to produce composites in which the mechanical properties were isotropic in the plane of the sample and approached the property limits predicted by composite theory. Additionally, it was found that many of the mechanical properties of the VB/PP materials were greatly enhanced by the addition of a maleated PP throughout the composite forming process.

This part of work was concerned with the processing of pellets of polypropylene (PP) containing pregenerated microfibrils of thermotropic liquid crystalline polymers (TLCPs), referred to as microcomposites. The microcomposites were produced by drawing strands of PP and TLCPs generated by means of a novel mixing technique and pelletizing the strands. The work was undertaken in an effort to improve on the properties observed for in situ composites in which the TLCP fibrils are generated in elongational flow fields that occur during processing.

In situ composites usually exhibit highly anisotropic mechanical properties and the properties do not reflect the full potential of the TLCP fibers. Factors considered include the effect of in situ composite strand properties on the properties of the injection molded composite, the melt temperature used in the injection molding, TLCP concentration, and the melt temperature of the TLCP.

It was found that microcomposites can be processed by means of injection molding, sheet extrusion, and extrusion blow molding. It was necessary to process the materials at low temperatures to maintain the TLCP fibrils. However, HX6000, the higher melting TLCP allowed higher processing temperatures than Vectra A. When the TLCP fibrils were maintained, the properties of the TLCP reinforced composites did show reduced anisotropy as compared to an in situ composite. The tensile strength of the composites produced by all three methods was about equal. The modulus of the injection molded composites was slightly higher than that of the composite sheets, but the composite sheets showed a lower degree of mechanical anisotropy. In all three processing methods the modulus of the TLCP reinforced composite was a function of the modulus of the in situ composite strand used to produce the microcomposite. Therefore, it is recommended that to improve the properties of the microcomposites the properties of the

in situ composite strands should be improved. Furthermore, the mechanical properties of the composites increased with increasing TLCP composition.

To provide a basis of comparison the properties of extruded sheets and the injection molded composites were compared to both the predictions of composite theory and the properties of glass reinforced composites. It was found that the modulus of the 10 wt% composites approached the predictions of composite theory, but at higher TLCP loadings the modulus showed negative deviations from the predictions of composite theory. This is believed to be the result of a reduction of fiber aspect ratio due to poor fiber distribution and fiber breakup. The modulus of the TLCP reinforced composites was about the same as the modulus of glass reinforced composites produced by both sheet extrusion and injection molding. The tensile strengths were slightly lower than that of the glass reinforced composites. It is expected that as the modulus and strength of the reinforcing TLCP fibrils are improved the properties of the TLCP reinforced composites should exceed those of glass reinforced composites. It was concluded that the processing of microcomposites is a viable means of producing composites based on TLCPs and thermoplastics with good mechanical properties and low degrees of mechanical anisotropy.

- * The Effect of Compatibilization on the Properties of Blends of Thermotropic Liquid Crystals with Polypropylene, by H.J. O'Donnell et al.
- * Thermoplastic Composites Based on Blends of Polypropylene with Liquid Crystalline Polymers, by H.J. O'Donnell

Processing Studies of In Situ Composites Based on Blends of Liquid Crystalline Polymers with Engineering Thermoplastics, by J.P. de Souza et al.
- * Effect of Deformation History on the Morphology of Blends of Liquid Crystalline Polymers with Thermoplastics, by A.M. Sukhadia and D.G. Baird
- * The Effect of Miscibility on the Morphology and Properties of Blends of Polyetherimide with Liquid Crystalline Polymers, by S.S. Bafna et al.
- * Miscibility and Mechanical Properties of Polyetherimide/Polyetheretherketone/Liquid Crystalline Polymer Ternary Blends, by R.E.S. Bretas and D.G. Baird
- * Mechanical Properties of In Situ Composites Based on Partially Miscible Blends of Polyetherimide and Liquid Crystalline Polymers, by S.S. Bafna et al.
- * Mechanical Properties of In Situ Composites Based on Partially Miscible Blends of Glass-Filled Polyetherimide and Liquid Crystalline Polymers, by S.S. Bafna et al.
- * The Effect of Compatibilization on the Properties of In Situ Composites Based on Polypropylene and Liquid Crystalline Polymer, by Arindam Datta et al.

The Effects of Compression Molding and Drawing on the Mechanical Anisotropy of In Situ Thermoplastic Composites, by J.P. de Souza and D.G. Baird

The Effect of Compatibilization on Blends of Polypropylene with a Liquid Crystalline Polymer, by Arindam Datta et al.

The Role of Partial Miscibility on the Properties of Blends of a Polyetherimide and Two Liquid Crystalline Polymers, by S.S. Bafna et al.

- * In Situ Reinforcement of Polypropylene with LCP: Effect of Maleic Anhydride Grafted Polypropylene, by H.H. O'Donnell and D.G. Baird

- * The Effect of Injection Molding Conditions on the Mechanical Properties of an In Situ Composite: I. Polypropylene and a LCP Based on HBA/HNA, by H.J. O'Donnell and D.G. Baird
- * The Effect of Injection Molding Conditions on the Mechanical Properties of an In Situ Composite: II. Polypropylene and a Copoly(Ester-Amide), by H.J. O'Donnell and D.G. Baird
- * The Effect of Injection Molding Conditions on the Mechanical Properties of an In Situ Composite: III. Polypropylene and a Copolyester LCP Based on PET/PHB, by H.J. O'Donnell and D.G. Baird
- * Compatibilization of Thermoplastic Composites Based on Blends of Polypropylene with Two Liquid Crystalline Polymers, by Arindam Datta and Donald G. Baird

The Effect of Compatibilization and Mixing on the Mechanical Properties of a Polypropylene/TLCP Blend, by H.J. O'Donnell et al.

Compression Molding of Drawn Polypropylene Vectra A Strands, by A.A. Handlos and D.G. Baird

The Development of Morphology in Blends of a Thermotropic Liquid Crystalline Polymer and Polypropylene: A Comparison of Mixing History by E. A. Sabol and D. G. Baird, accepted for publication in International Polymer Processing.

Composites Based on Drawn Strands of Thermotropic Liquid Crystalline Polymer Reinforced Polypropylene, by E. A. Sabol, A. A. Handlos, and D. G. Baird, accepted for publication in Polymer Composites.

Injection Molding of Microcomposites Based on Polypropylene and Thermotropic Liquid Crystalline Polymers, by A. A. Handlos and D. G. Baird, submitted to International Polymer Processing.

Sheet Extrusion of Microcomposites Based on Thermotropic Liquid Crystalline Polymers and Polypropylene, by A. A. Handlos and D. G. Baird, submitted to Polymer Composites.

Extrusion Blow Molding of Microcomposites Based on Thermotropic Liquid Crystalline Polymers and Polypropylene, by A. A. Handlos and D. G. Baird, submitted to Polymer Composites.

STUDENTS SUPPORTED:

- A.A. HANDLOS (Ph.D. completed September 1994)
- J.P. de SOUZA (Ph.D. completed January 1994)